

Metal contents in *Porites* corals: Anthropogenic input of river run-off into a coral reef from an urbanized area, Okinawa

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Abstract

In order to monitor pollutants from urban areas to coral reefs, metal contents in *Porites* coral samples collected from the Hija River mouth and at nearby sites from the estuary were analyzed. The corals were cleaned by oxidative and reductive treatments to effectively eliminate detritus and organic materials. Metal-to-calcium (Me/Ca) ratios in the samples were determined by ICP-MS. Filtered samples of river water were also measured similarly for metal concentrations. The extent of anthropogenic contribution by riverine input was assessed by comparing the Me/Ca values in corals to those of Rukan-sho, an unpolluted coral reef. High riverine inputs of Mn, Cd, Zn and Ag were observed from Me/Ca values in the coral samples. Manganese in the coral samples showed strong dependence on salinity, varying inversely to the distance from terrestrial sources. Considering a lead background of 25.0 nmol/mol measured in the Rukan-sho corals, Pb/Ca in corals of the Hija River estuary that are two and three times higher may indicate lead enrichment in the river mouth. Because Pb is only moderately high in the Hija River water compared to its concentration in surface seawater, lead may have accumulated in the estuarine water and sediments, resulting in an elevated concentration of lead available for coral uptake.

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Keywords: Coral; Metals; *Porites*; Okinawa; Manganese; Lead

1. Introduction

Rivers are subject to discharges of wastewater as an inevitable result of urbanization. Untreated sewage coming from domestic and industrial sources are transported from the rivers to the estuary, carrying pollutants like heavy metals. The adverse effects of these pollutants is evident in the coastal environment, e.g. reduced biodiversity, diminished production and even death of certain corals. Although there are marine species that can thrive under relatively high metal concentrations (Miao et al., 2001), the difference in species-specific response due to biochemical utility or toxicity (Esslemont et al., 2000) may prove deleterious to other life stages in which low metal concentrations can significantly affect the fertilization process (Reichelt-Brushett and Harrison, 1999, 2000). Pollution including sewage and heavy metals may contribute to the collapse of reef ecosystems adjacent to the river mouth and lead

to the loss of estuarine habitats (Zann, 2000). As well, riverine transport is regarded as an important pathway for input of nutrients to the coastal environment. Riverine nutrient loads of nitrogen, phosphorus and silica has been known to limit biological primary production. For example, phosphate deficiency in coastal areas could preclude the dominance of diatoms in the phytoplankton community (Egge, 1998). Because river discharge is a major source of both nutrients and heavy metal pollutants, it is appropriate to measure the chemical composition of rivers and estuarine areas, in the interest of pollution monitoring. Several studies have been carried out to assess the metal content of river water, colloidal particles and sediments in estuary (Banat and Howari, 2003; Jain and Sharma, 2001; Klavin et al., 2000; Munksgaard and Parry, 2001; Ramessur and Ramjeawon, 2002).

Sediments are chemical fossils which record global and local environmental changes. However, the record from sediment data could be altered by human activities such as dredging and processes like remineralization and recrystallization. In a study of heavy metals in seawater, marine sediments and corals, Esslemont et al. (2000)

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noted that in some measurements, metal availability as represented by metal in coral skeleton, may have been inadequately represented by sediment data. Corals are deemed to be very useful indicators of pollution level because their skeletons assimilate records of certain metals over hundreds of years (Esslemont, 1999). The composition of coral skeleton reflects the extent of pollution caused by heavy metals or nuclear wastes (Scott, 1990). *Porites* corals, for example, can function as recorders of mining and environmental impacts (Fallon et al., 2002; David, 2003). A comparison with the natural background of the area can then provide the basis for identifying influences of local human activities on coral reefs.

During the formation of CaCO_3 , metal ions are taken up by the aragonite lattice, according to an ion-exchange reaction, i.e. $\text{CaCO}_3 + \text{Me}^{2+} = \text{MeCO}_3 + \text{Ca}^{2+}$. The metal-to-calcium (Me/Ca) ratio of coral aragonite is mainly controlled by three factors: (1) the distribution coefficient of the metal ion between aragonite and seawater, (2) the $\text{Me}^{2+}/\text{Ca}^{2+}$ ratio of the surface oceanic water, and (3) biological effects.

Me/Ca ratios in corals may be documented to evaluate aquatic environmental conditions in which the corals grew. Pb/Ca ratios in corals, for example, has been used as a chemical tracer to evaluate the availability of lead. Shen and Boyle (1987) showed that Pb/Ca in coral skeleton increased in the 1940s due to the use of leaded fuels for motor vehicles. Bastidas and Garcia (1999) have also confirmed that Pb/Ca ratio can be applied as a recorder of marine pollution from anthropogenic activities. In order to assess lead contamination due to rapid development near a coastal area, Medina-Elizalde et al. (2002) measured lead chronology in the coastal environment using Pb/Ca ratio in scleractinian coral. Similarly, other Me/Ca ratios in corals may be used to extend the pollution assessment to other metals present in the ambient seawater.

Coral reefs are widely distributed in the islands of Okinawa, Japan. In Okinawa, nutrients are supplied to the reefs from forests of the hinterland and clean seawater flows to this region by tidal actions and the Kuroshio stream. Such forces that lead to gain and loss of nutrients serve to balance the ecology of the coral community. The ecological balance is disturbed by land-use changes and associated river discharges (West and van Woesik, 2001) that contain sediments contaminated by trace metals (Elbaz-Poulichet et al., 1984; Bastidas et al., 1999). The transition from the river mouth to a point where the effect of river discharge is minimal has been assessed using a method called moving window analysis (West and van Woesik, 2001). Such method was applied to the coral reef near the Hija River mouth, with the idea that the distance from the river mouth to the transition point is determined by the extent of pollution from the river, i.e. transition extends farther from the

estuary when pollution level increases. West and van Woesik (2001) reported a transition zone of 400 m from the Hija River mouth.

To understand the anthropogenic impact of metals in the coastal environment, it is critically important to study river transport and discharge to the estuary and to analyze the metal contents in reefs adjacent to the river mouth. This survey of the Hija River estuary builds on the work of West and van Woesik (2001) by providing metal pollution data as reinforcement to the diffusion model that they developed for this river. In this paper, we report the observations that were performed on a coral reef in Okinawa based on the measurement of metal contents in river water and nearby coral skeletons.

2. Materials and methods

2.1. Study location

Okinawa is located at $26^{\circ}25'N$ and $128^{\circ}00'E$ (Fig. 1a), with a human population of over a million people (1 130 682, from Japanese National Census Data, 1994). The population density of Okinawa varied widely from 7500 persons km^{-2} in southern Okinawa to 34 persons km^{-2} in the northern region (West and van Woesik, 2001).

The Hija River, the largest river in Okinawa, has a catchment area of 50.2 km^2 . Its maximum discharge is 43.04 $\text{m}^3 \text{s}^{-1}$. In 1994, the population density in the nearest surrounding area of this river was 900–5000 people km^{-2} .

The sampling sites were designated from upstream of the river towards the estuary and to nearby coastal areas. Points from left and right sides of the river were designated as sampling sites, starting from the hinterland to the ocean (Fig. 1b). Sites 1–5 comprise the sources of samples that were taken from the left side while sites 7–11 represent the right side. Corals were found to survive between sites 1–11, as shown in Fig. 1c.

To provide as reference for a relatively pristine, uncontaminated coral community, samples were also taken from site 14, Rukan-sho (see Fig. 1a). Rukan-sho, an isolated Okinawan island, is a small atoll that has a rich coral reef fauna and flora (Ohde and van Woesik, 1999).

2.2. Sample

Coral, seawater and river water samples were collected for the study.

On 5 and 6 July 2000, coral samples were collected from sites 6, 12 and 13 (Fig. 1b). On 16 September 2000, coral samples were also obtained from sites 1–5 and 7–11, as shown in Fig. 1c. Seawater samples were taken from the same sites by skin diving and were stored in

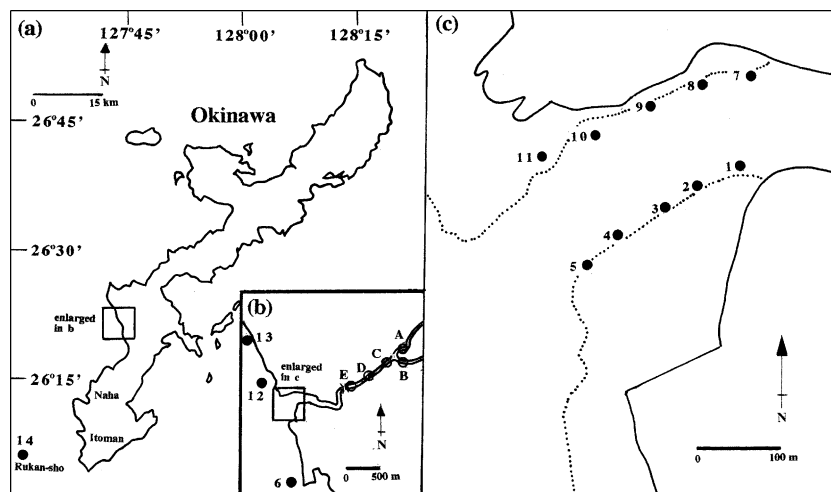


Fig. 1. (a) Map showing the location of Okinawa (Japan) and Rukan-sho site. (b) Sampling sites of coral specimens (6, 12 and 13) marked with filled circles and sampling sites of river water (A–E) indicated by open circles, (c) Diagram of the Hija River estuary showing sampling sites 1–5 and 7–11. Continuous dots indicate the coral reef edge.

polyethylene bottles. Seawater was collected for each month from September to November 2000.

The Hija River flows downstream from the center of Okinawa Island to the East China Sea, passing through Okinawa City and the Kadena US Air Force Base. Fig. 1b marks the sampling sites of river water, labeled A–E. There were small mangroves near the river mouth area between C and E. River water samples were collected from the five sites on 2 September, 29 October 2000, 20 and 25 January 2001.

Coral samples from the reference site, Rukan-sho, were collected on 3 July and 25 October 1999.

2.3. Analytical methods

Massive *Porites* corals (~10–20 cm) were cut into 5 mm slices using a diamond saw. The slices were washed with milli-Q water, and placed in a sonic bath for 10 min. After drying the slices, about 0.5 mm of the surface was cut off by a dental drill. Then the surface of the sliced sample (5 mm thick) was cut by small diamond saw for analysis. The sample was cleaned in sonic bath using milli-Q water, covered by Teflon sheet and was ground using an agate mortar. About 1–1.5 mg powdered sample was taken in a 1.5 ml centrifuge tube and weighed. Milli-Q water was added into the sample tube and the mixture was centrifuged for 10 min. The sample was then washed repeatedly with 1.0 ml of milli-Q water in the sonic bath for 10 min.

Shen and Boyle (1987) proposed an oxidative and reductive cleaning procedure of coral skeleton to remove surface contamination, incorporated sediments and symbiotic zooxanthellae. We used their method to measure only metals bound onto the carbonate lattice. Their cleaning procedure was employed on the powdered

samples. Each of the cleaned samples was dissolved in 1 ml of 1% HNO_3 and was left overnight for complete dissolution. After dissolution, the sample was centrifuged for 10 min and the dissolved sample was transferred into Teflon beaker to dilute it to 7 ml sample solution using 1% HNO_3 . This 7 ml of final solution was used in ICP-MS measurement. The diluted sample solution contained calcium ion of ~100 ppm. Then the ratio of metal to calcium was measured using ICP-MS. We used ICP-MS (Hewlett Packard, HP 4500) to measure 15 elements (Na, Mg, Al, Ca, Mn, Zn, As, Sr, Y, Ag, Cd, Ba, Pb, Th and U). These metal contents were determined by the calibration method.

After filtration of river water, concentrated (68%) HNO_3 was added with it to adjust the solution as 1% HNO_3 solution for ICP-MS measurement. Seawater salinity was determined by a salinometer (YEO-KAL, 601 MK111, Australia) using the standard seawater of IAPSO ($K_{15} = 0.99985$, $S = 34.994$). Chloride concentration in river water was measured by AgNO_3 titration.

3. Results and discussion

Analytical results are given in Tables 1–4. Table 1 provides a list of the salinity data for seawater from the Hija River estuary, including water temperature, sampling depth and time. The concentrations of the metals and chloride in river water at the sampling sites A–E (Fig. 1b) are listed in Table 2. Table 3 gives the mean metal concentrations of river water at sites A and B, and literature values of metal concentration in the North Pacific surface seawater compiled by Nozaki (1997). Metal/calcium ratios in coral skeletons are summarized in Table 4.

Table 1
Salinity of estuarine water collected from the Hija River mouth

Sampling site	July 6, 2000	August 11, 2000	August 12, 2000	September 3, 2000	October 29, 2000	November 29, 2000
1	–	34.250 psu (0.5 m) (28.0 °C, 10:10)	–	32.423 psu (30.0 °C, 15:32)	32.707 psu (28.0 °C, 13:25)	34.060 psu (24.0 °C, 12:50)
2	–	33.993 psu (0.5 m) (28.0 °C, 10:30)	33.737 psu (30.0 °C, 14:10)	–	–	–
3	–	34.198 psu (0.5 m) (28.0 °C, 11:30)	–	29.734 psu (29.3 °C, 15:25)	33.457 psu (28.0 °C, 13:30)	34.237 psu (24.0 °C, 12:55)
4	–	33.648 psu (0.5 m) (28.0 °C, 12:00)	–	31.726 psu (29.3 °C, 15:15)	3.961 psu (27.5 °C, 13:35)	34.363 psu (23.9 °C, 13:00)
5	–	–	33.238 psu (29.0 °C, 14:00)	32.840 psu (28.5 °C, 15:10)	34.225 psu (27.8 °C, 13:40)	34.431 psu (23.8 °C, 13:10)
6	34.639 psu (4 m) (27.0 °C, 17:40)	–	–	–	–	–
7	–	–	18.114 psu (30.0 °C, 14:20)	25.347 psu (29.5 °C, 16:40)	34.048 psu (28.4 °C, 13:15)	27.759 psu (24.0 °C, 13:35)
8	–	–	21.052 psu (29.5 °C, 14:50)	25.944 psu (29.5 °C, 16:50)	33.630 psu (28.0 °C, 13:10)	30.002 psu (23.9 °C, 13:30)
9	33.074 psu (0.3 m) (27.0 °C, 18:20)	–	–	24.844 psu (29.3 °C, 16:55)	–	–
10	34.250 psu (0.3 m) (27.0 °C, 18:00)	–	31.071 psu (29.5 °C, 10:30)	–	33.973 psu (29.5 °C, 13:05)	29.604 psu (23.8 °C, 13:25)
11	33.971 psu (0.3 m) (27.0 °C, 18:00)	–	33.435 psu (26.5 °C, 10:00)	–	34.162 psu (27.8 °C, 13:00)	31.863 psu (23.8 °C, 13:20)
12	34.532 psu (1.5 m) (27.0 °C, 17:15)	–	–	–	–	–
13	34.587 psu (0.5 m) (28.2 °C, 15:00)	–	–	–	–	–

(–): not determined.

No depth information: 0.1 m.

Sampling sites are shown in Fig. 1.

Numbers in parentheses indicate water temperature, sampling depth and time.

3.1. Salinity change in the Hija River estuarine

Salinity data provide information on mixing between river water and seawater. The sampling program for the collection of river water and estuarine water samples in this study was based on the monthly report provided by the Okinawan Weather Station. Sampling was carried out at low tide conditions and around full moon or new moon phase. In all times of sample collection, there was no rainfall, even in the few days prior to the sampling dates, except on August 3, 2000, when rainfall was reported to be 6.0 mm on August 2, 2000.

With the exception of salinity measurements at sites 7, 8 and 9, salinity range was essentially restricted to a narrow range of ~30–35 (Table 1). On the left side of the estuary, salinity was rather uniform except on September 3, 2000, when inter-site differences on salinity was more pronounced. On the right shore, salinity values showed a wider variability compared to salinity measurements on the left shore. Sites 1, 7, 8 and 9 had salinity values that were markedly lower than those at the other sites, and this was evident in September 3, 2000. However, similarity in salinity data at the estuarine sites on July 6 and August 12, 2000 suggests a fairly well-mixed estuarine water.

3.2. Water chemistry of the Hija River

Metals in river water are derived from two main processes. One is natural dissolution processes which include weathering. The other is due to human activities (anthropogenic processes). In order to estimate the extent of metal pollution from anthropogenic activities, it is essential to characterize the Hija River in terms of its background metal content. The chemistry of the river water is vital in this assessment, in the sense that point sources of metals could be identified.

The influence of seawater's mixing with the Hija River water is remarkable from site C, as indicated by the significantly higher chlorine values recorded from that site and downstream, compared with those of freshwater inputs coming from sites A and B (Table 2). At site C, the major constituents of seawater such as Ca, Na, Mg and Sr proportionally increased with increased salinity. A similar trend in concentration at sites C, D and E suggests the conservative nature of these elements in seawater. In contrast, Mn, Y, Ag, Ba, Pb and Th behaved non-conservatively. The concentrations of Al and Zn showed less variability compared to those of the other trace metals. Cadmium concentrations are notably high and showed high variability in relation to the actual

Table 2
Chemical composition of river water collected from the Hija River

Site (sampling date)	Cl (mg/kg)	Ca (mg/kg)	Na (mg/kg)	Mg (mg/kg)	Al (µg/kg)	Mn (µg/kg)	Zn (µg/kg)	As (µg/kg)	Sr (mg/kg)	Y (ng/kg)	Ag (ng/kg)	Cd (ng/kg)	Ba (µg/kg)	Pb (ng/kg)	Th (ng/kg)	U (ng/kg)
<i>August 3, 2000</i>																
C	–	77.7	Over	44.3	10.8	50.0	3.13	2.51	0.415	40.5	52.0	221	11.3	131	–	–
D	–	83.6	Over	Over	9.88	41.8	4.17	3.49	0.553	34.5	50.6	229	9.50	81.4	–	–
<i>September 2, 2000</i>																
A	34.9	69.3	23.8	5.62	13.8	62.7	2.61	1.41	0.176	33.5	56.8	298	14.3	137	55.1	714
B	38.4	69.0	21.4	5.75	11.6	45.6	1.52	1.75	0.184	26.0	55.2	299	15.0	87.9	29.6	906
C	1680	78.3	Over	43.5	11.6	50.9	3.20	2.64	0.425	45.0	–	352	13.3	201	50.3	1010
<i>October 29, 2000</i>																
A	44.0	55.3	16.4	4.80	17.9	97.6	0.928	1.05	0.142	21.8	30.4	115	12.6	26.0	55.7	570
B	45.4	55.6	17.8	5.01	21.1	90.1	1.01	1.22	0.148	16.9	25.3	104	13.2	22.8	97.0	749
C	3830	89.6	Over	Over	24.2	75.3	–	9.18	1.36	18.3	–	130	7.31	28.1	63.0	675
<i>November 29, 2000</i>																
A	41.9	47.9	16.2	4.22	13.8	26.1	1.74	0.529	0.111	25.3	24.1	107	9.28	34.6	475	335
B	45.4	58.7	17.4	5.17	8.28	37.7	1.24	0.959	0.142	21.2	23.7	106	12.3	44.4	248	770
C	4680	125	Over	Over	5.56	23.4	–	13.2	1.81	15.7	8.36	71.9	–	14.2	19.7	586
D	4850	126	Over	Over	5.80	20.4	–	12.7	1.71	17.4	12.0	71.1	–	20.2	35.6	563
E	5160	125	Over	Over	5.73	25.9	–	12.7	1.77	15.1	10.1	67.2	–	24.1	90.0	578
<i>January 20, 2001</i>																
A	–	47.3	22.3	4.32	11.6	30.3	1.23	0.471	0.0994	22.3	7.68	19.5	7.09	74.2	7.63	84.7
B	–	50.4	18.6	5.00	11.8	37.3	1.52	0.947	0.145	15.0	4.09	4.65	9.80	72.5	8.54	84.7
<i>January 25, 2001</i>																
A	–	45.7	21.6	4.19	11.3	29.3	1.20	0.485	0.0959	20.3	6.58	21.9	6.88	77.9	6.50	84.7
B	–	51.7	19.2	5.20	12.7	38.1	1.61	0.962	0.149	15.0	4.59	6.21	10.0	67.3	6.20	84.7

(–): not determined.

Over: could not be determined.

Sampling sites A, B, C, D, E are shown in Fig. 1.

Table 3

Average metal concentrations of the Hija river water and literature values of the North Pacific surface water

Metal, unit	Site A (average $\pm 1\sigma$)	Site B (average $\pm 1\sigma$)	Seawater ^a
Na (mg/kg)	20.1 \pm 3.5 (16.2–23.8)	18.9 \pm 1.6 (17.4–21.4)	10,800
Mg (mg/kg)	4.63 \pm 0.61 (4.19–5.62)	5.23 \pm 0.31 (5.00–5.75)	1280
Al (μ g/kg)	13.7 \pm 2.6 (11.3–17.9)	13.1 \pm 4.8 (8.28–21.1)	0.088
Mn (μ g/kg)	49.2 \pm 30.9 (26.1–97.6)	49.8 \pm 22.8 (37.3–90.1)	0.036
Zn (μ g/kg)	1.54 \pm 0.67 (0.928–2.61)	1.38 \pm 0.25 (1.01–1.61)	0.0046
As (μ g/kg)	0.789 \pm 0.423 (0.471–1.41)	1.17 \pm 0.35 (0.947–1.75)	0.67
Sr (mg/kg)	0.125 \pm 0.034 (0.0959–0.176)	0.487 \pm 0.740 (0.145–1.81)	7.9
Y (ng/kg)	24.6 \pm 5.3 (20.3–33.5)	18.8 \pm 4.7 (15.0–26.0)	8.0
Ag (ng/kg)	25.1 \pm 20.5 (6.58–56.8)	22.6 \pm 20.8 (4.09–55.2)	0.5
Cd (ng/kg)	112 \pm 113 (19.5–298)	104 \pm 120 (4.65–299)	0.16
Ba (μ g/kg)	10.0 \pm 3.3 (6.88–14.3)	12.1 \pm 2.1 (9.80–15.0)	4.8
Pb (ng/kg)	69.9 \pm 44.0 (26.0–137)	59.0 \pm 25.5 (22.8–87.9)	13
Th (ng/kg)	120 \pm 200 (6.50–475)	77.9 \pm 102.0 (6.20–248)	0.014
U (ng/kg)	358 \pm 284 (84.7–714)	519 \pm 401 (84.7–906)	3400

Numbers in parentheses indicate the concentration range.

^a Based on the compilation of Nozaki (1997).

concentrations reported in Table 2. Silver concentrations in river water decreased throughout the duration of sampling.

As shown in Table 3, the concentrations of Th, Mn, Cd, Zn, Al and Ag in river water were much higher than those in the surface seawater (North Pacific Ocean). To a lesser extent, Pb, Y, Ba and As river water concentrations were also high compared with those in seawater. U concentrations at sites A and B were rather low compared to the literature values for U from the surface seawater. Based on these comparisons of metal concentrations in the Hija River water to those in the Pacific Ocean's surface water, the following inferences are made: The Hija River water is (a) highly enriched in Th, Mn, Cd, Zn, Al and Ag; (b) slightly enriched in Pb, Y, Ba and As; and (c) not a significant source of U. These inferences are made for the purpose of establishing the metal input from the river. Here we assume that the metal concentrations supplied by the river water during the dates and times of sampling, are representative of their concentrations in the previous months, during the growth of the coral samples. Coral skeletal growth rate is ~ 1 mm/month.

As the metals are carried by river water to the river mouth, their concentrations could be modified by various physical and chemical processes in the estuary. Mixing of river water and seawater at the estuary results in flocculation which precipitates a large amount of the dissolved metals supplied by the river (Gerringa et al., 2001). Trace metals like Mn, Al and Cd, are removed from the solution by estuarine flocculation (Sholkovitz, 1978).

In the Hija River estuary, biological oxygen demand (BOD₅) and suspended particulate matter (SPM) have been reported to be 3.2 ± 2.8 mg/l and 6.2 ± 4.4 mg/l, respectively (West and van Woesik, 2001). These values are the average measurements for 20 years (1976–1996) recorded on a monthly basis by the Okinawa Prefectural Department of Public Health. These BOD₅ and SPM levels for the Hija River estuary are relatively low compared to those of other Okinawan rivers (West and van Woesik, 2001). The uniformly low BOD₅ and SPM values may suggest a correspondingly low level of bacteria in the estuarine water as well as low nutrient levels. Given the range in water temperature (24–30 °C), the concentration of dissolved oxygen is approximately 8 mg/l, or 100% oxygen saturation, which is consistent with the low BOD₅ and SPM values. However, the level of dissolved oxygen may decrease with the rise in temperature and salinity seaward. As the salinity increases, dissolved nutrients and organic matter from the river water may settle in the estuary and accumulate on the bottom sediments. The build-up and consequent decomposition of organic wastes coming from sewage and urban run-off utilize oxygen from the water column. Measurements of dissolved oxygen in the samples could have provided data on the variations in oxygen saturation in the context of the increasing salinity from upstream sites to the estuary.

Resuspension of bottom sediments and particulate matter could provide adsorption sites to the trace metals, which could effectively lower the dissolved metal concentration at the river mouth. Fe and Al tend to form colloidal particles that bind metals (Wood et al., 1995). The occurrence of diagenetic reactions in marine sediments could also significantly affect the river water composition and lead to concentration gradients. In order to monitor such water chemistry, we collected coral samples and determined metal-to-calcium ratios in the samples.

3.3. *Me/Ca in coral*

Fig. 2a–n shows the metal-to-calcium ratios in *Porites* corals collected from the Hija River sites and those from Rukan-sho. For each site from 1 to 14, the mean and standard deviation of two data (from two coral samples) are plotted. As shown in the figures, As, Mn, Zn, Ag, Pb and U had generally higher concentrations in the sites

Table 4

Me/Ca (mole ratio) in a frame of *Porites* coral collected from the Hija River estuary (sites 1–13) and Rukan-sho (site 14)

Site	Sample code	Na/Ca (10 ⁻³)	Mg/Ca (10 ⁻³)	Al/Ca (10 ⁻⁶)	Mn/Ca (10 ⁻⁶)	Zn/Ca (10 ⁻⁶)	As/Ca (10 ⁻⁶)	Sr/Ca (10 ⁻³)	Y/Ca (10 ⁻⁶)	Ag/Ca (10 ⁻⁹)	Cd/Ca (10 ⁻⁹)	Ba/Ca (10 ⁻⁶)	Pb/Ca (10 ⁻⁹)	Th/Ca (10 ⁻⁹)	U/Ca (10 ⁻⁶)
1	00081101	18.6	3.68	16.1	2.87	34.3	1.03	8.08	84.7	163	625	1.74	42.3	48.4	1.00
	00081103	18.1	3.70	3.29	2.98	10.8	0.015	8.40	74.6	116	130	2.20	48.4	47.4	0.707
2	00081214	18.0	5.04	1.88	2.31	7.86	0.104	9.92	35.8	138	70.8	9.34	73.5	244	0.923
	00081215	18.5	4.11	0.886	1.91	29.8	0.171	9.71	43.1	79.1	42.4	4.54	43.2	122	1.02
3	00081104	18.2	4.60	1.74	2.56	22.8	0.108	9.20	46.4	61.3	6.68	3.39	29.9	72.6	0.959
	00081105	18.9	5.02	1.89	2.51	7.91	0.152	9.70	36.6	83.4	30.8	9.54	33.2	29.9	0.825
4	00081106	18.8	4.58	1.25	1.66	15.9	0.225	9.23	52.2	77.6	39.9	13.6	38.2	2.7	0.813
	00081211	19.0	5.16	0.798	1.56	6.41	0.271	9.17	54.5	95.5	66.0	8.85	26.5	1.4	0.782
5	00081212	18.4	3.98	0.881	0.984	20.3	0.356	9.60	42.2	86.4	47.5	2.24	31.0	33.1	0.941
	00081213	18.6	3.70	1.32	0.848	4.53	0.258	9.64	41.7	117	94.5	6.05	36.5	29.8	0.970
6	00070503	18.1	3.87	1.60	0.345	6.60	0.146	8.87	63.6	26.3	16.0	11.5	31.2	29.8	0.745
	00070504	17.3	3.48	0.75	0.304	5.79	0.082	9.01	48.0	13.2	31.4	2.41	34.8	32.7	0.277
7	00081208	18.6	3.64	41.3	7.58	9.58	0.292	9.35	106	92.3	88.0	4.11	76.1	13.4	1.05
	00081210	19.4	4.60	0.901	3.60	14.9	0.173	9.23	53.2	15.2	143	4.17	30.8	16.0	0.744
8	00081209	18.7	3.83	1.15	5.57	8.02	0.541	9.53	33.1	96.3	209	2.66	27.5	12.5	0.961
	00081207	18.2	3.75	2.43	1.87	8.02	1.07	7.74	66.6	183	727	1.89	17.9	36.4	0.802
9	00081205	16.7	4.00	12.8	3.03	5.64	0.006	7.93	49.7	146	21.1	2.37	56.2	83.1	1.15
	00081206	19.4	3.96	32.3	3.16	3.43	0.041	7.89	56.4	108	30.1	4.68	59.4	97.0	1.02
10	00081203	16.5	3.91	2.89	2.16	2.30	0.008	8.35	42.3	52.1	8.96	3.13	21.9	27.0	0.903
	00081204	18.8	3.81	9.86	2.05	6.43	0.037	7.86	30.8	62.7	23.0	3.63	36.7	37.6	0.998
11	00081201	17.4	4.22	1.88	1.53	24.5	0.759	7.74	58.0	156	578	1.65	14.5	21.5	0.732
	00081202	18.1	4.42	4.87	1.15	20.2	0.744	8.08	61.5	149	498	7.83	19.2	20.8	0.727
12	00070604	20.2	4.14	5.15	0.600	2.60	0.015	8.27	35.3	29.6	14.2	2.92	23.1	21.9	0.916
	00070605	18.2	4.79	4.75	1.50	4.10	0.027	8.32	41.2	15.1	12.3	2.53	26.1	16.3	0.899
13	00070601	18.7	3.65	0.806	0.172	2.21	0.107	9.04	54.3	19.8	58.0	8.26	20.5	18.2	0.873
	00070602	19.4	4.06	1.83	0.569	5.96	0.145	10.2	23.0	32.4	17.8	6.54	22.5	59.8	0.954
14	990703021	17.4	3.51	1.02	0.220	0.261	0.037	9.14	49.6	17.8	19.7	5.88	27.6	46.4	0.827
	991025011	18.6	4.64	0.668	0.125	0.267	0.075	8.75	49.5	14.7	14.0	4.31	22.5	29.4	0.661

Sample code shows sampling date (e.g. 00081101: 11 August 2000).

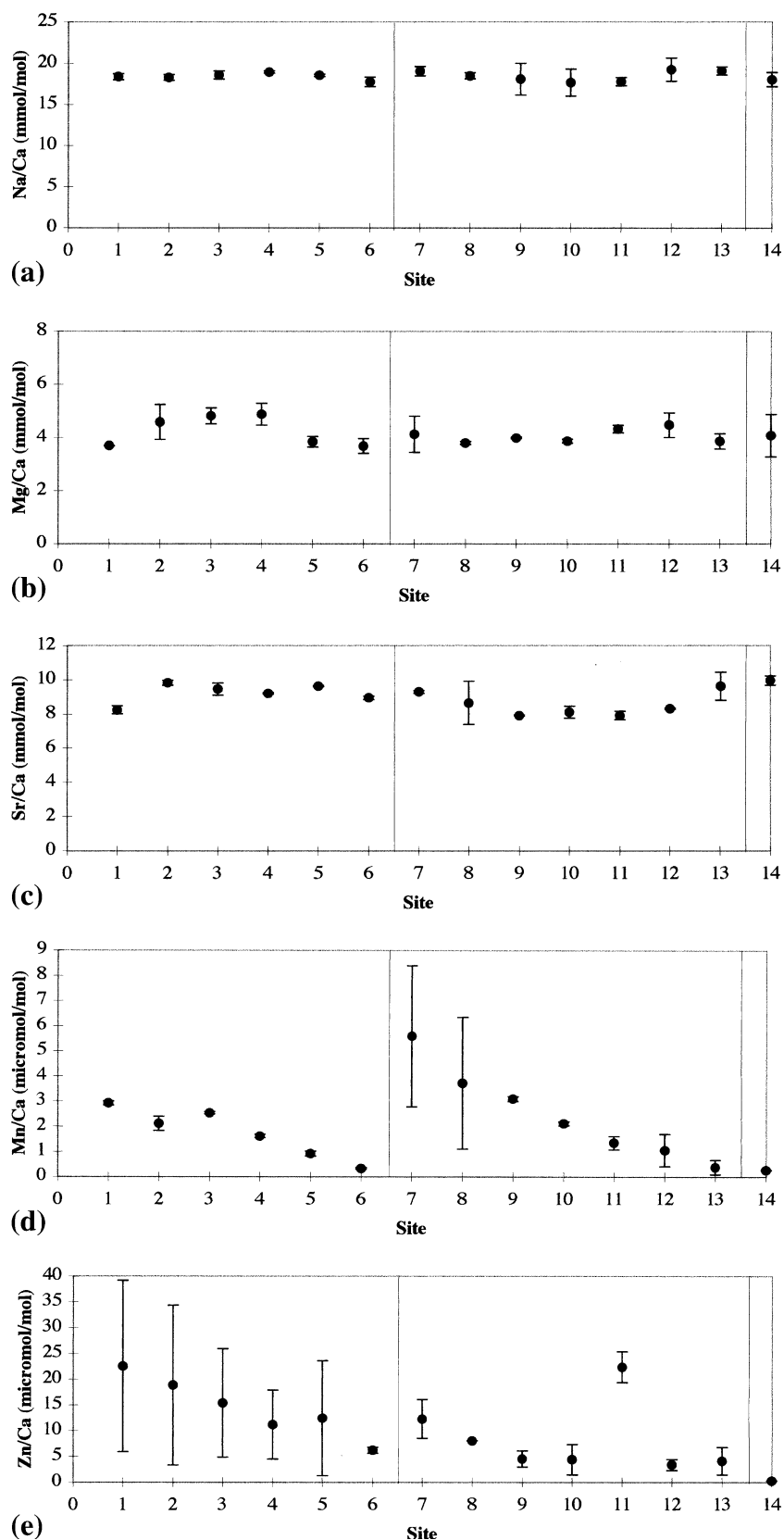


Fig. 2. Metal-to-calcium ratios in *Porites* coral samples taken from sites 1–6 (left shore) and 7–13 (right shore) of the Hija River estuary and Rukan-sho (site 14). Two coral samples from each site were collected to determine (a) Na/Ca, (b) Mg/Ca, (c) Sr/Ca, (d) Mn/Ca, (e) Zn/Ca, (f) Ag/Ca, (g) Pb/Ca, (h) Al/Ca, (i) As/Ca, (j) U/Ca, (k) Ba/Ca, (l) Cd/Ca, (m) Th/Ca and (n) Y/Ca. The graphs show the mean and standard deviation for Me/Ca values from two corals analysed at each site. The maximum analytical error for each measurement is less than 5%.

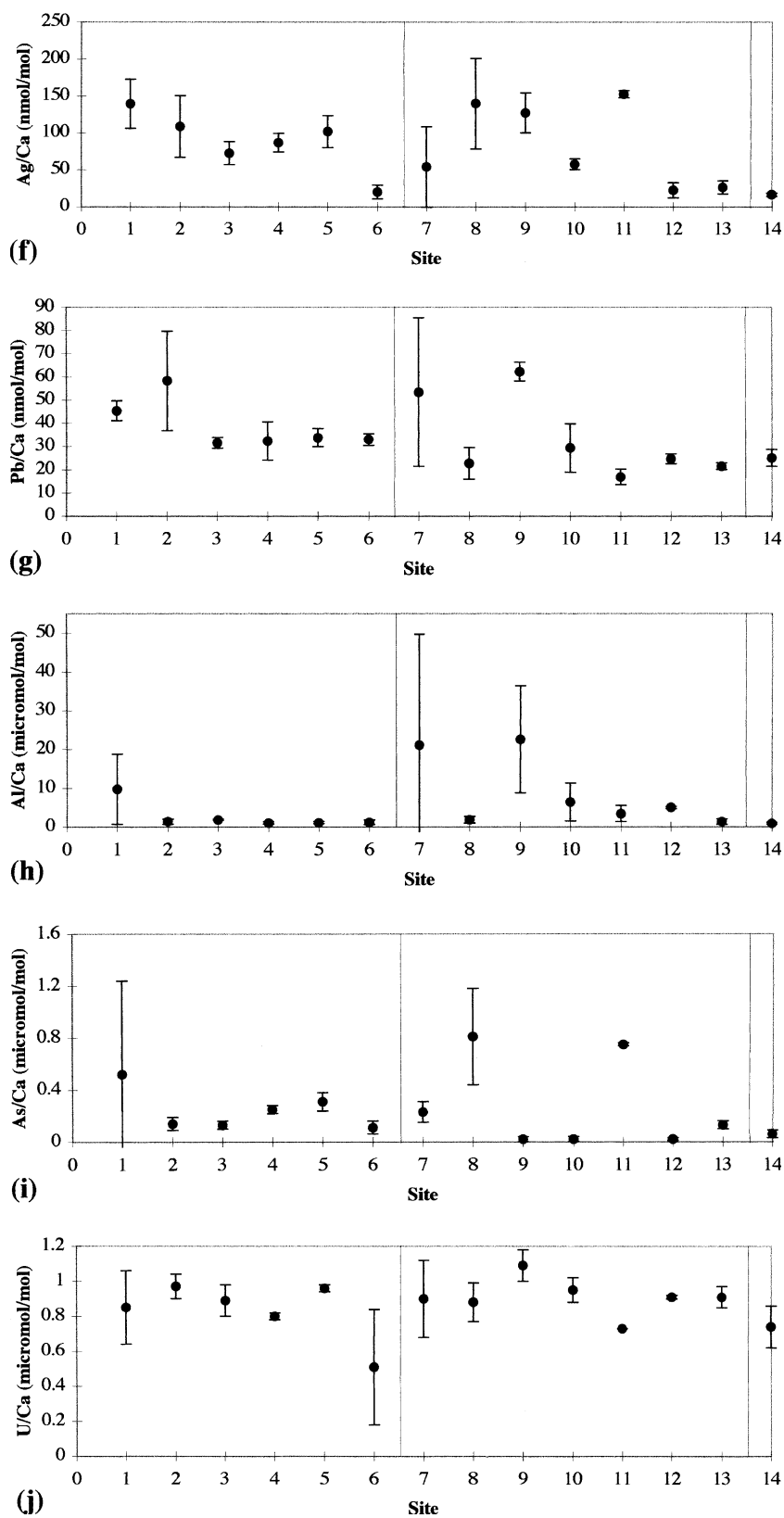


Fig. 2 (continued)

investigated in the Hija River, compared to the Rukan-sho values. Their Me/Ca ratios showed wide ranges in

variability within and/or among sites. The samples were characterized by highly variable concentrations of Zn

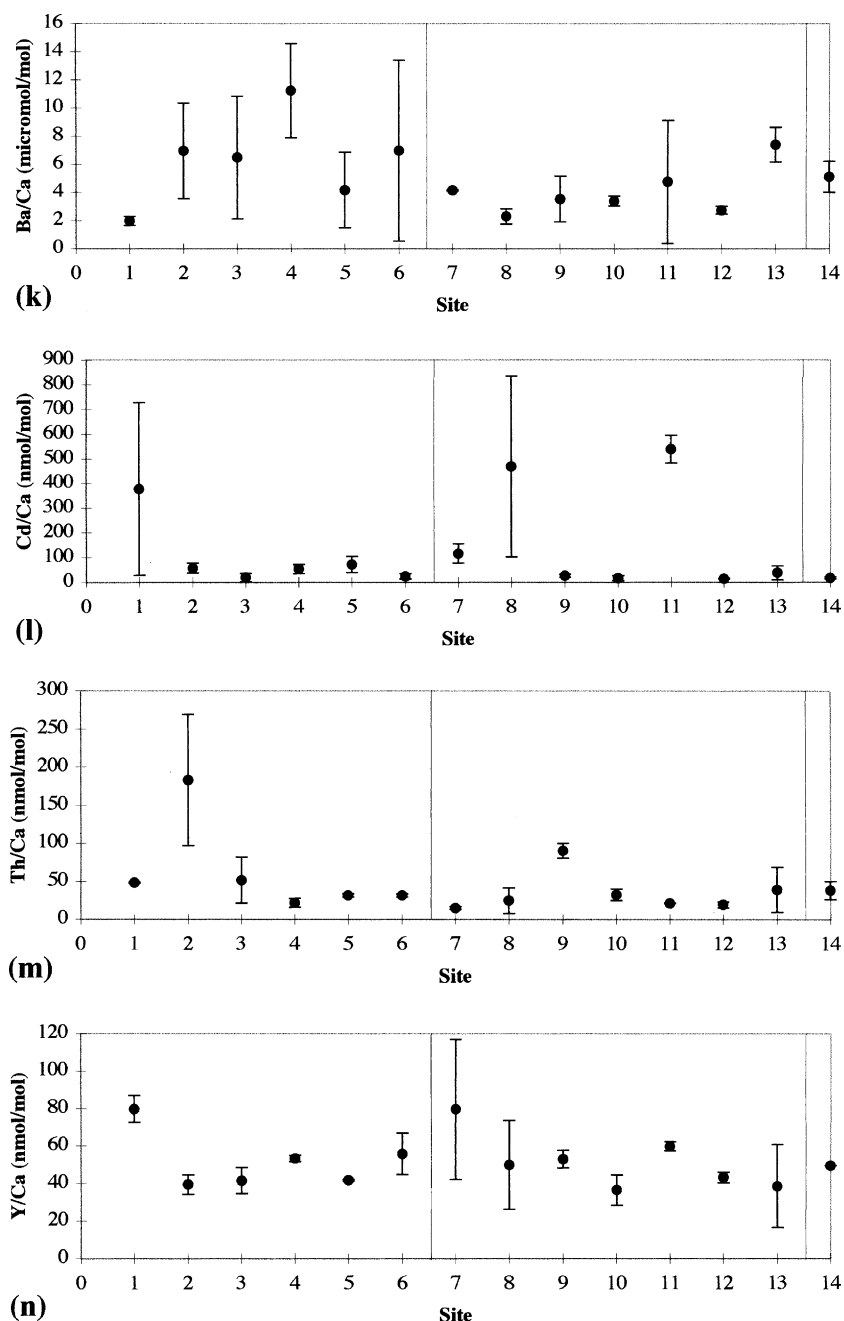


Fig. 2 (continued)

and Ba (especially on the left shore), and to a lesser extent Ag. On the other hand, Na, Sr and Mg displayed more consistency in Me/Ca ratios compared to the rest of the metals. Th, Y, Cd and Ba have Me/Ca values that are comparable to or slightly higher than the Rukan-sho values. These metals possibly showed slight anthropogenic contributions. Further discussion also delves into the assessment of metal contents in the coral samples relative to the metal concentrations in river water. This assessment is based on the assumption that there has been no significant changes in the metal concentrations

of the river water, from the growth and formation of the coral samples to the time of river water and coral sampling.

3.4. Na/Ca, Mg/Ca and Sr/Ca

Na, Mg and Sr are conservative major elements in seawater and they are uniformly distributed in the world's oceans (Stumm and Morgan, 1981). Fig. 2a–c shows the Na/Ca, Mg/Ca and Sr/Ca (mole ratios) in the coral samples, respectively, as listed in Table 4. The

figures indicate that the three elements had essentially uniform Me/Ca ratios of corals which are in good agreement with the Rukan-sho values. Mean coral values of 18.4 mmol Na/mol Ca, 4.14 mmol Mg/mol Ca and 8.85 mmol Sr/mol Ca at the estuarine are also consistent with the corresponding Rukan-sho ratios. Due to the conservative nature of Na, Mg and Sr in seawater, the constant Na/Ca, Mg/Ca and Sr/Ca in the corals is attributed to seawater effect. Swart (1981) has reported that Mg/Ca in scleractinian coral skeletons is affected by growth rate of the coral, and that Na/Ca in coral could be influenced by salinity. In the Hija River estuary, inter-site differences in growth rate may have been negligible, resulting in uniform Mg/Ca values in the corals. The narrow range of salinity at the river mouth may have led to similarity in Na uptake by the corals. Strontium partitioning in corals is known to depend on seawater temperature, thus the application of Sr/Ca ratio as paleothermometer. Seawater temperature was also monitored in the present study (Table 1) but the temperature data from the river mouth may not suffice to explain the small inter-site differences in Sr/Ca in the coral samples.

3.5. Mn/Ca, Zn/Ca and Ag/Ca

Mn, Zn and Ag displayed very strong anthropogenic overprints, as can be gleaned from Fig. 2d, e and f, respectively. The corals reflected the high river water concentrations of Mn, Zn and Ag (Table 3). This observation is in accord with the idea that coral skeletons record ambient trace-metal concentrations that reflect river discharge (Shen and Sanford, 1990).

Mn/Ca ratios in the coral skeletons showed a remarkable decreasing trend on both sides of the river. At the left shore, Mn/Ca values varied from 2.87 and 2.98 $\mu\text{mol/mol}$ in site 1 to 0.98 and 0.85 $\mu\text{mol/mol}$ in site 5. On the other side of the river, values ranged from 1.53 and 1.15 $\mu\text{mol/mol}$ in site 11 to 7.58 $\mu\text{mol/mol}$ in site 7. As expected, the decreasing behavior extends to sites 6, 12 and 13 due to seawater dilution. Values at sites 6 and 13 are comparable to Rukan-sho values (0.22 and 0.13 $\mu\text{mol/mol}$).

The high concentrations of Mn could be due to a great terrigenous influence in the area. With a Mn distribution coefficient between aragonite and seawater (D_{Mn}) of 0.1 (Shen and Boyle, 1988), Mn appears to be discriminated against by other metals. The possibility of incorporation is reduced with lower concentrations nearer the seashore.

The decreasing trend in Mn/Ca ratios may be explained by the non-conservative mixing behavior of Mn in the Hija River estuary. This non-conservative behavior of Mn is consistent with the presence of high amount of suspended matter in the river mouth. Furthermore, the extent of mixing could possibly account

for the distribution of Mn, which was the only element that displayed a significant decrease in concentration with small increase in salinity (which were taken under similar tidal conditions, Table 1). Mn may be sensitive to slight increases in salinity values, leading to enhanced coagulation or adsorption to suspended matter as salinity values approach 35. Assuming that under similar tidal conditions, the salinity data here are representative of the salinity of the estuarine water at the sites where the corals grew, the increase in salinity to values approaching 35 from sites 1–6 and sites 7–13 (Table 1) apparently correspond to the decrease in Mn/Ca ratios from river mouth to estuary to farther coastal areas. As shown in Table 1, salinity measurements at sites 7 and 8 on 12 August 2000 (a month before and after the collection of coral samples), which were 18 and 21, respectively, might have contributed to the higher Mn/Ca in those sites compared to the rest of the sampling points. This observation supports the behavior of Mn with salinity changes in Tamar Estuary, as reported by Knox et al. (1981). The observed maximum in Mn concentration at salinities around 20 may be due to the mixing of interstitial water rich in manganese into the water column (Knox et al., 1981), with Mn (II) as the dominant form. The removal of Mn (II) from the solution as salinities approach 35 could be the result of heterogeneous adsorption/oxidation processes, with the high concentration of suspended particulate matter (Knox et al., 1981; L'her Roux et al., 1998). These adsorption/oxidation processes favor the formation of colloidal Mn. Based on the results, it may be argued that manganese in corals displays a sensitivity that makes it an effective indicator of seawater conditions, i.e., salinity changes and manganese ion concentration.

As shown in Fig. 2e, the Rukan-sho coral also serves as a pollution indicator of zinc in the Hija River area. The highest concentration of zinc was recorded at site 1 (34.3 $\mu\text{mol/mol}$), which is much higher than the Rukan-sho values (0.261 and 0.267 $\mu\text{mol/mol}$). Zinc is enriched in the coral skeleton relative to seawater (distribution coefficient $D_{\text{Zn}} = 11$; Shen and Boyle, 1988). It is therefore more preferentially taken up by the growing aragonite crystal, compared to manganese.

Record of coralline Ag content show considerable pollution at the study sites, excluding the Ag/Ca values at sites 6, 12 and 13. High Ag/Ca values in most of the sites confirm the importance of human activities as a source of Ag contamination. Photographic processing may still be a significant source of Ag even if there has been a shift from using analog to digital machines in the past two decades. Releases from the photographic industry in the past could have accumulated in soils, along with sewage discharge. Silver in soil could be mobilized by erosion and find its way to the river water and estuarine. Combustion of fossil fuels such as oil and coal,

could also emit Ag particles that may be taken by the river through rainfall.

3.6. *Pb/Ca, Al/Ca, As/Ca, U/Ca*

Fig. 2g–j shows the Pb/Ca, Al/Ca, As/Ca and U/Ca mole ratios in the coral samples, respectively. It is apparent from Fig. 2g that lead contamination is high at sites 1, 2, 7, and 9. Lead may substitute directly for calcium in the aragonite lattice. With a Pb distribution coefficient between aragonite and seawater of $D_{\text{Pb}} = 2.3$ (Shen and Boyle, 1988), lead is highly concentrated in the coral skeleton compared to the surrounding water. As shown in Table 3, high Pb concentration from Nagara River (69.9 ng/kg) and Hija River (59.0 ng/kg) is decreased downstream but it slightly increases again at site E, just under the Hija Bridge (24.1 ng/kg), as might have been anticipated due to water run-off from the highway. This water run-off from the highway results from lead-containing car emissions that may be deposited on the road, which can be washed away by rain and mixed with river water. The phasing out of Pb-alkyl fuel additives might have reduced recent anthropogenic inputs of Pb but a substantial amount of petrol lead residing in soil along roads in the area may be eroded to accumulate in the estuarine environment (De Carlo and Anthony, 2002).

Elevated Pb/Ca values in corals at sites 2 and 7, were two and three times higher than the average Rukan-sho value (25.0 nmol/mol). The figures show values from two corals analyzed at each site and these high values are not consistent between the duplicates. Such observation is noted for most of the other metals investigated here. These results suggest high variability between colonies at sites that may be polluted. For Pb/Ca, the peak values may indicate that the coral reefs at the estuary are suffering from chronic anthropogenic lead input. The long-term effect of river discharge could be a high degree of lead accumulation at the river mouth, leading to prolonged exposure. Moreover, the contribution of atmospheric Pb coming from automobile exhausts could have also elevated the Pb content in the river mouth. Lead isotopic tracing can possibly provide a more extensive distinction between Pb from the natural background, from car exhausts and from industries (Bing-Quan et al., 2001).

Most of the coral samples recorded Al contents that were similar to those of Rukan-sho which has a mean Al/Ca of 0.844 $\mu\text{mol/mol}$. This observation does not support the presence of high Al input from the river. With the exception of measurements from sites 1 (16.1 $\mu\text{mol/mol}$), 7 (41.3 $\mu\text{mol/mol}$) and 9 (12.8 and 32.3 $\mu\text{mol/mol}$), estuarine precipitation of Al and formation of Al particulates could have diminished dissolved Al for coral uptake.

Arsenic in the corals was considerably high in sites 1 (1.03 $\mu\text{mol/mol}$), 8 (0.541 $\mu\text{mol/mol}$) and 11 (0.759 and

0.744 $\mu\text{mol/mol}$) compared with Rukan-sho As/Ca ratios of 0.037 and 0.075 $\mu\text{mol/mol}$ (site 14). However, for most of the sites in the estuary, As/Ca in corals were slightly higher than or comparable to those of Rukan-sho. This general observation is consistent with the data on river water As concentration, which is also slightly higher than that of the surface seawater.

Uranium overprint is evident at sites 1 (1.00 $\mu\text{mol/mol}$), 8 (0.961 $\mu\text{mol/mol}$) and 11 (0.730 $\mu\text{mol/mol}$). Except samples taken from site 12, corals found farther from the river mouth (sites 6 and 13) were also moderately high in U relative to the Rukan-sho reference. Shen and Boyle (1988) suggested that beyond direct substitution of metals, U ($D_{\text{U}} = 0.6\text{--}1.0$) can be skeletally incorporated and the uranyl carbonate complex may actually replace CaCO_3 groups in the lattice. However, they did not explain the mechanism of replacement. With the premise that uranyl carbonate complex substitutes for CaCO_3 in the aragonite lattice, U/Ca in coral skeletons, therefore, depends not only on the uranyl ion concentration but also on the carbonate system. Uranium is known to desorb from colloids when the pH of seawater increases. The concentration of carbonate ion also increases with seawater pH, which in turn is influenced by CO_2 uptake for photosynthesis. Therefore, an increase in pH (alkalinity) favors the formation of uranyl carbonate complex, which translates into an increased U uptake by corals. Moreover, although there has been a decrease by more than half in the U river water concentration at site C during the sampling period, accumulated uranium in the sediments at the estuarine area may redistribute to the surrounding water.

3.7. *Ba/Ca, Cd/Ca, Th/Ca and Y/Ca*

The samples were characterized by highly variable concentrations of Ba, especially on the left shore (Fig. 2k). Barium is regarded as a valuable tracer delivered to the oceans by rivers (Shen and Sanford, 1990). The high Ba/Ca values at sites 2 (9.34 $\mu\text{mol/mol}$), 3 (9.54 $\mu\text{mol/mol}$), 4 (8.85 and 13.6 $\mu\text{mol/mol}$), 11 (7.83 $\mu\text{mol/mol}$) and 13 (8.26 and 6.54 $\mu\text{mol/mol}$), are greater than the Rukan-sho values (5.88 and 4.31 $\mu\text{mol/mol}$) and led to wider range in the values. High Ba concentrations may be partly due to the storage of sediments in freshwater sections of the river mouth during high discharge. Slightly high barium input from the river coupled with the reworking of sediments deposited in freshwater Ba might have enhanced the concentrations in the estuary, leading to high Ba coral content.

Cd/Ca were also generally similar to the Rukan-sho values (Table 4, 19.7 and 14.0 nmol/mol), except in sites 1 (625 nmol/mol), 7 (143 nmol/mol), 8 (727 nmol/mol) and 11 (578 and 498 nmol/mol) which are rather high. The higher Cd/Ca values in coral may reflect the high

amount of Cd input from the river. It has been reported that Cd in estuarine and coastal waters shows a strong positive correlation to salinity (Munksgaard and Parry, 2001). Gerringa et al. (2001) also reported that Cd concentrations in the estuary increase with increasing salinity due to the formation of chloride complexes and by adsorption on suspended particles. In terms of Cd content in corals, such observation corresponds to increased Cd uptake of coral with higher salinities. We observed that higher Cd/Ca ratios were recorded in corals of the upper estuary at sites 1, 7 and 8. It should be noted, however, that Cd/Ca at site 11 was also high (see Fig. 2l), and that site 2 has a similar salinity to site 1 but with considerably lower Cd/Ca ratio compared to that at site 1, an observation that weakens the relationship of Cd/Ca to salinity. Inconsistencies in the observed relation of Cd/Ca in coral to salinity may be attributed to biologic factors (such as differences in rate of coral growth and zooxanthellar activity) and influence of the underlying sediments (in scavenging for cadmium in seawater). A data logger at some sites would have provided a more relevant and extensive set of salinity data. Furthermore, the limited range in salinity data in this study makes it difficult to establish a strong Cd to salinity correlation.

Cd chemistry has been closely correlated with that of zinc because of their similar electronic structures. In this study, both Cd and Zn had high concentrations in river waters compared with those in surface seawater (Table 3). Anthropogenic sources of Cd could come from nickel–cadmium batteries, plastic stabilizers and solders. Sources of zinc include alloys, dyes, automobile tyres, paints and galvanizing materials. Our observations that the corals were high in Zn but low in Cd, despite the fact that both Zn and Cd were very high in the river waters compared to their concentrations in surface seawater, is ascribed to the higher tendency of Cd than that of Zn to bind to colloidal particles. Cd removal at the estuary must have occurred through adsorption on colloids and particulate matter.

The corals also recorded moderate impacts of thorium (Fig. 2m) and yttrium (Fig. 2n). Th contamination is observed at sites 2 and 9. Y impact is notable at sites 1 and 7. However, for most of the sites, Th/Ca and Y/Ca were similar to Rukan-sho values. Generally, the results do not justify the high concentrations of both Th and Y at sites A and B. These two metals may have low distribution coefficient values in *Porites* corals.

4. Conclusions

The following tentative conclusions are derived from the observations of the Hija River estuary in an effort to monitor metal pollutants from urban areas to coral reefs. Riverine input from human activities was estimated by

comparing the coral metal contents at the estuary to those of Rukan-sho, taken as a reference for baseline metal concentrations.

- (a) The study sites of the Hija River mouth showed high Mn, Zn, Ag and Pb in *Porites* corals compared with those in Rukan-sho corals. The coral samples apparently reflected the enrichment of river water in these metals. The coral samples also recorded slight anthropogenic inputs of Th, Y, Cd and Ba. Coral skeletons may be used as indicators of environmental availability for some metals. Inconsistent Me/Ca values in corals recorded at the same sites suggest high variability at sites that may be polluted.
- (b) Taking into account the low river water concentrations of uranium compared to that in surface seawater, and the distribution coefficient of U between aragonite and seawater, it is possible that elevated U in the aragonite lattice is associated with remobilisation of accumulated U in the river mouth as well as an increase in alkalinity of estuarine water. Such conditions favor the formation of uranyl carbonate complex, thus increasing the concentration of the complex available for coral uptake.
- (c) Among all the metal-to-calcium ratios investigated, only Mn/Ca showed a decreasing trend from higher to lower estuary. The estuary had salinity values that were mainly restricted to a range of 30–35. The strong dependence of Mn on salinity change was explained by its non-conservative behavior. Elevated Mn concentrations at salinities around 20 could possibly arise from desorption reactions, and removal at the lower estuary where salinities approach 35 may be the consequence of adsorption/oxidation processes.
- (d) High lead uptake by the corals amounting to two and three times the baseline level measured at Rukan-sho, could be the result of lead released from estuarine sediments, from road and river run-off, and from atmospheric input.

Based on the observations, the reef environment of the Hija River mouth may be adversely affected by long-term continuous metal input from Okinawa City through the Hija River. Although coral record could be modified by reactions in estuaries, corals could possibly provide a useful fingerprint of riverine discharge of metals.

Acknowledgements

We thank R. Shinjo for his help in the ICP-MS analysis. T. Ono provided assistance in the graphics. We are also grateful to R. van Woesik and an anonymous referee for their critical reviews of drafts of this manuscript. This

work was partly supported by the Japanese Ministry of Education and Science through JSPS, and the Sumitomo Foundation.

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